Evaluation of Uncertainties in Atomic Data on Spectral Lines and Transition Probabilities

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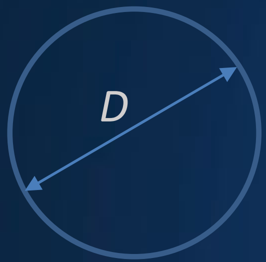
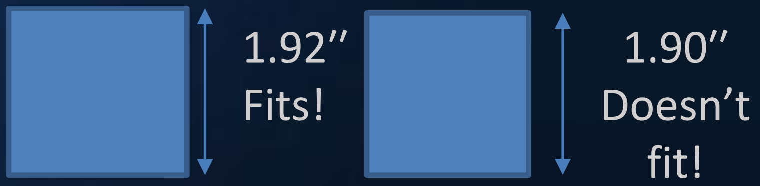
Introduction: “data” vs “numbers”



Ratio of circumference to diameter:
$L / D = \pi$, $\pi = 3.1415...$ is a *number*

Measurement *data* for *D*:
1.9005 ± 0.0005
1.9001 ± 0.0005
1.9010 ± 0.0005
1.9008 ± 0.0005
1.9003 ± 0.0005

Mean: 1.90054 ± 0.00022 (inch)



Uncertainty is intrinsic part of data and cannot be omitted

Uncertainties in wavelength measurements

Guides **for evaluating and expressing uncertainty in measurements**

GUM (BIPM): https://www.bipm.org/en/committees/jc/jcgm/publications
NIST TN1297: http://physics.nist.gov/TN1297
NIST TN1900: https://doi.org/10.6028/NIST.TN.1900
NUM: https://uncertainty.nist.gov/

Despite the availability of guides, uncertainty of a weighted mean is still controversial

Uncertainty of weighted mean: example

Measurement 1: G = 6.67430(15) [×10−11 m^3/(kg s^2)] – CODATA2018
Measurement 2: G = 6.690(3) [...] – Undergraduate physics experiment

Weighted mean (standard statistics): $v_{\mathrm{wm}} = \sum v_i w_i / \sum w_i\,, \quad w_i = 1/u_i^2$
Uncertainty of wm: $u_{\mathrm{wm}} = 1/\sqrt{\sum w_i}$

G_{wm} = 6.67434(15) [...] – "biased" uncertainty?

Unbiased unc. of wm (https://en.wikipedia.org/wiki/Weighted_arithmetic_mean):

$u_{\mathrm{biased}}^2 = \sum w_i (v_i - v_{\mathrm{wm}})^2 / V_1; \quad u_{\mathrm{unbiased}} = u_{\mathrm{biased}} / \sqrt{1 - V_2/V_1^2}$
$V_1 = \sum w_i; \quad V_2 = \sum w_i^2$

$u_{\mathrm{biased}} = 0.00080$ $\qquad u_{\mathrm{unbiased}} = 0.01100$ [...]

Error: WRONG STATISTICAL MODEL
The two measurements are *inhomogeneous*

Dark Uncertainties in Heterogeneous Measurements

Measurement 1: G = 6.67430(15) [×10−11 $m^3/(kg\ s^2)$] – CODATA2018
Measurement 2: G = 6.690(3) [...] – Undergraduate physics experiment

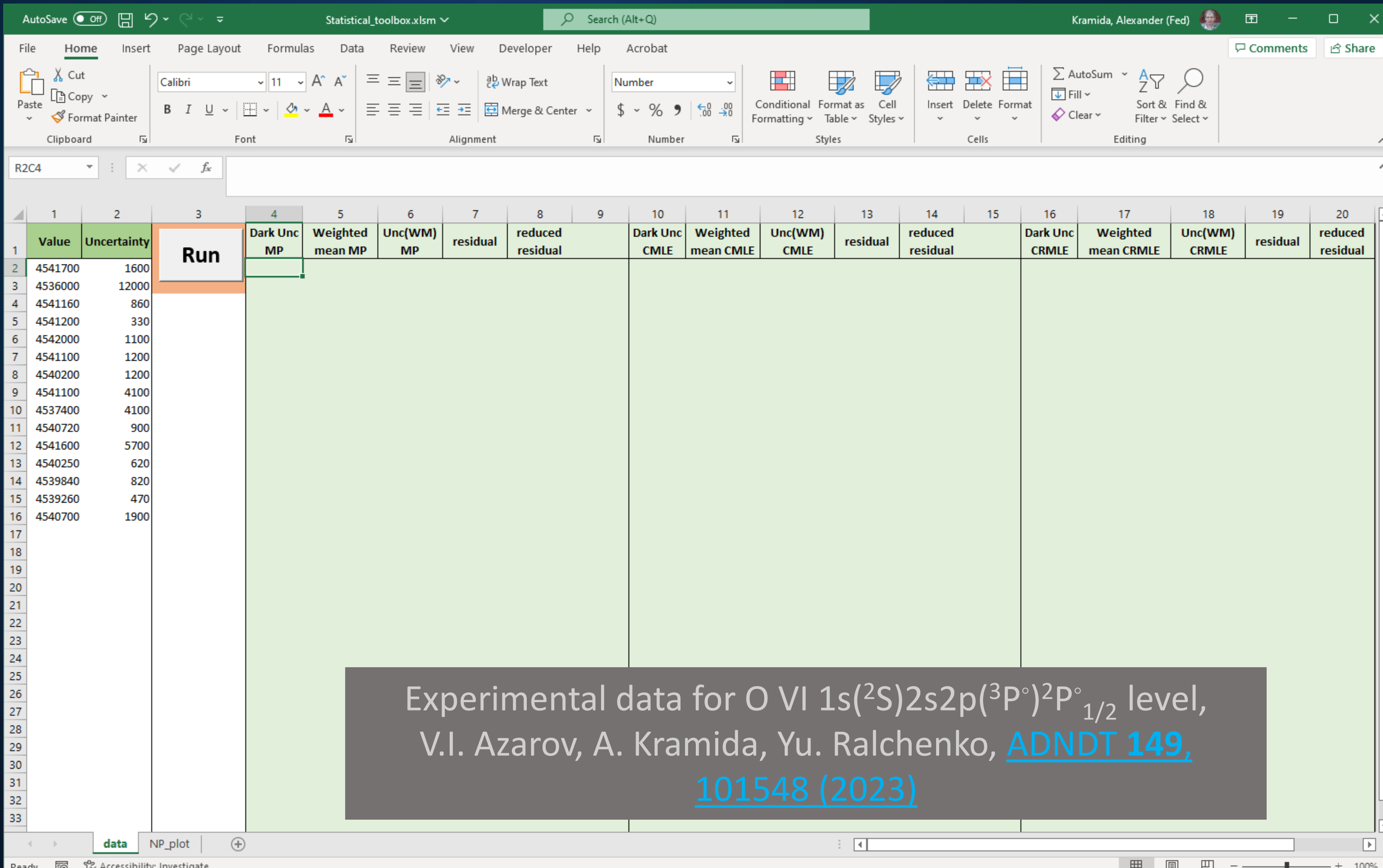
Weighted mean with dark unc.: $v_{\mathrm{wm}} = \sum v_i w_i / \sum w_i$, $w_i = 1/(u_i^2 + d_i^2)$
Uncertainty of wm: $u_{\mathrm{wm}} = 1/\sqrt{\sum w_i}$

A. L. Rukhin, Metrologia **56**, 035002 (2019):
Clustered Maximum Likelihood Estimator (CMLE)
Clustered Reduced Maximum Likelihood Estimator (CRMLE)

$d_1 = 0$, $d_2 = 0.016$ $\rightarrow G_{\mathrm{wm}} = 6.67430(15)$ [...] – Justice restored!

Wavelength measurements are *inhomogeneous*
(different line profiles, blending, Stark shifts, ...)

Statistical Toolbox



Value	Uncertainty	Dark Unc MP	Weighted mean MP	Unc(WM) MP	residual	reduced residual	Dark Unc CMLE	Weighted mean CMLE	Unc(WM) CMLE	residual	reduced residual	Dark Unc CRMLE	Weighted mean CRMLE	Unc(WM) CRMLE	residual	reduced residual
4541700	1600															
4536000	12000															
4541160	860															
4541200	330															
4542000	1100															
4541100	1200															
4540200	1200															
4541100	4100															
4537400	4100															
4540720	900															
4541600	5700															
4540250	620															
4539840	820															
4539260	470															
4540700	1900															

Experimental data for O VI $1s(^2S)2s2p(^3P^\circ)\,^2P^\circ_{1/2}$ level, V.I. Azarov, A. Kramida, Yu. Ralchenko, ADNDT **149**, 101548 (2023)

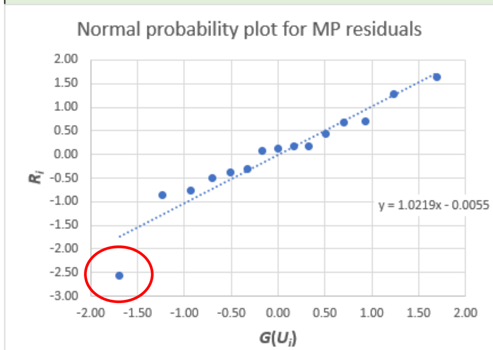
Statistical Toolbox

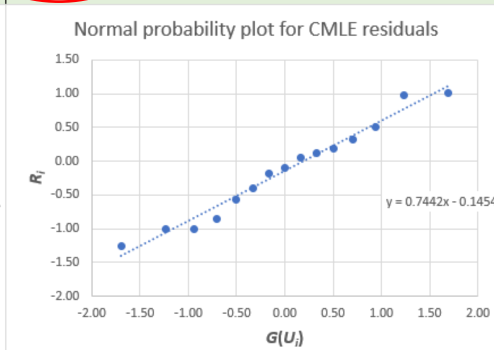
Statistical_toolbox.xlsm

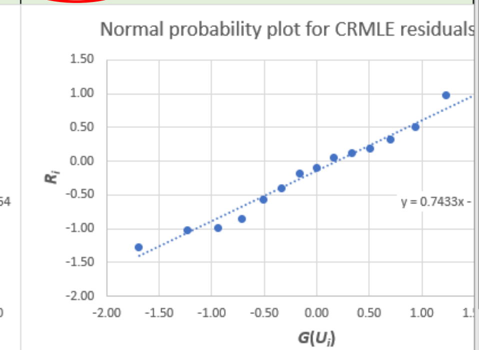
R15C10 | 1549.62240670951

Run

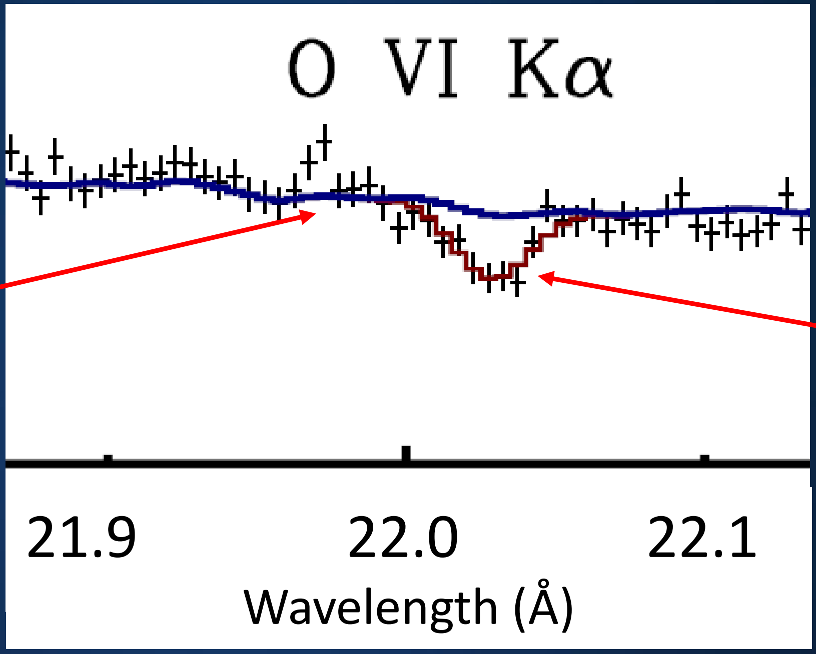
	Value	Uncertainty	Dark Unc MP	Weighted mean MP	Unc(WM) MP	residual	reduced residual	Dark Unc CMLE	Weighted mean CMLE	Unc(WM) CMLE	residual	reduced residual	Dark Unc CRMLE	Weighted mean CRMLE	Unc(WM) CRMLE	residual	reduced residual
2	4541700	1600	195	4540567	224	1133	0.70	0	4540879	228	821	0.51	0	4540880	228	820	0.51
3	4536000	12000	195			-4567	-0.38	0			-4879	-0.41	0			-4880	-0.41
4	4541160	860	195			593	0.67	0			281	0.33	0			280	0.33
5	4541200	330	195			633	1.65	0			321	0.97	0			320	0.97
6	4542000	1100	195			1433	1.28	0			1121	1.02	0			1120	1.02
7	4541100	1200	195			533	0.44	0			221	0.18	0			220	0.18
8	4540200	1200	195			-367	-0.30	0			-679	-0.57	0			-680	-0.57
9	4541100	4100	195			533	0.13	0			221	0.05	0			220	0.05
10	4537400	4100	195			-3167	-0.77	0			-3479	-0.85	0			-3480	-0.85
11	4540720	900	195			153	0.17	0			-159	-0.18	0			-160	-0.18
12	4541600	5700	195			1033	0.18	0			721	0.13	0			720	0.13
13	4540250	620	195			-317	-0.49	0			-629	-1.02	0			-630	-1.02
14	4539840	820	195			-727	-0.86	0			-1039	-1.27	0			-1040	-1.27
15	4539260	470	195			-1307	-2.57	1550			-1619	-1.00	1567			-1620	-0.99
16	4540700	1900	195			133	0.07	0			-179	-0.09	0			-180	-0.09







Physics of the outlying measurement



Part of the profile that was ignored

Measured part of the profile

Statistics can help to spot and localize the problem, but physics must be used to solve it.

Spotting outliers in "observed–Ritz" differences

FTS lines of Zr I and Zr II, J.E. Lawler, J.R. Schmidt, E.A. Den Hartog, JQSRT **289**, 108283 (2022)

σ_{obs}, cm^{-1}	$N_{spectra}$	E_{low}	E_{upp}	$\Delta\sigma_{obs-Ritz}$	DU_{MP}	DU_{CMLE}
14473.2603(15)	4	11016.6440	25489.8995	0.0048	0.0051	0.0062
14604.5628(15)	4	10885.3362	25489.8995	−0.0005	0.0051	0.0000
21303.8870(26)	3	4186.0080	25489.8995	−0.0045	0.0051	0.0000
25489.8915(25)	2	0.0000	25489.8995	−0.0080	0.0051	0.0062

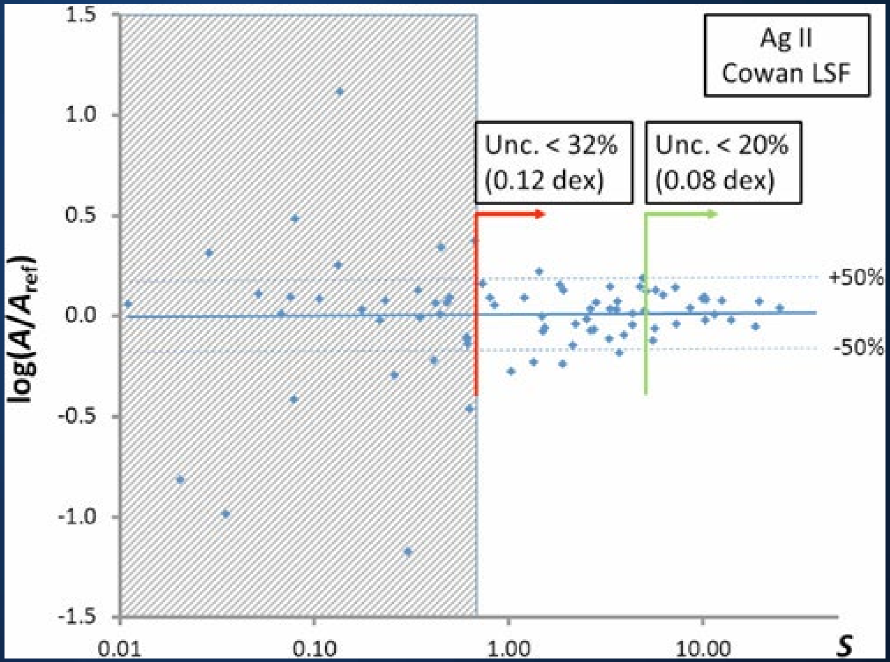
Treat as measured quantity with same uncertainties as σ_{obs}

Do not blindly add dark uncertainties to observed ones.
This does not eliminate physical errors and may accentuate them.

Uncertainties in calculated transition probabilities

Use line strength *S* as discriminating quantity.

A. Kramida, Fusion Sci. Technol. **63**, 313 (2013); Atoms **2**, 86 (2014)



Problem: line strength *S* is not always the best discriminating quantity to correlate with uncertainties

Comparison of length and velocity forms

C. Froese Fischer, Phys. Scr. **T134**, 014019 (2009)
J. Ekman, M.R. Godefroid, H. Hartman, Atoms **2**, 215 (2014)
GRASP2018: C. Froese Fischer, G. Gaigalas, P. Jönsson, J. Bieroń, CPC **237**, 184 (2019)

Uncertainty *indicator*

$$dT = \frac{|A_l - A_v|}{\max(A_l, A_v)}$$

Caveats:

- *dT* is not uncertainty! Only an indicator that must be treated statistically. Too often, $A_l \approx A_v$ but both are wrong!
- Because of max() in denominator, *dT* always underestimates uncertainties. **Better use min()**.

Better indicator of uncertainty

A. Kramida, Fusion Sci. Technol. **63**, 313 (2013)
F. El-Sayed, JQSRT **254**, 107204 (2020)

$$dL = \ln(S_1/S_2)$$

S_1 and S_2 are any two forms of line strength of the same transition.

Uncertainty in *S*:

$$u_S \approx e^{\langle dL \rangle} - 1$$

Caveat:

Neither *dT* nor *dL* are statistically justified: their statistical distributions are not normal. $\left[\left(\frac{S_1}{S_2}\right)^{\frac{1}{3}} - 1\right] / \left(\frac{1}{3}\right)$ may be better.

A. Kramida, Atoms **2**, 86 (2014)

Dividing transitions into groups: Which parameter does not depend on energy?

Similar S?	A. Kramida, Fusion Sci. Technol. **63**, 313 (2013)
Similar gA?	M.C. Li, W. Li, P. Jönsson et al., ApJS **265**, 26 (2023)
Similar gf?	W. Li, A.M. Amarsi, A. Papoulia et al., MNRAS **502**, 3780 (2021)
Similar branching fraction?	J.Q. Li, C.Y. Zhang, G. Del Zanna et al., ApJS **260**, 50 (2022)
Similar cancellation factor?	*No clear example*

I.P. Grant, J. Phys. B **7**, 1458 (1974)

Magnetic transitions (L is multipolarity: 1 for dipole, 2 for quadrupole, etc.):

$$S^{\mathrm{m}}_{\alpha\beta} \propto \left[\int_0^\infty (P_\alpha Q_\beta - Q_\alpha P_\beta) r^L \,\mathrm{d}r\right]^2$$

Electric transitions, Babushkin gauge:

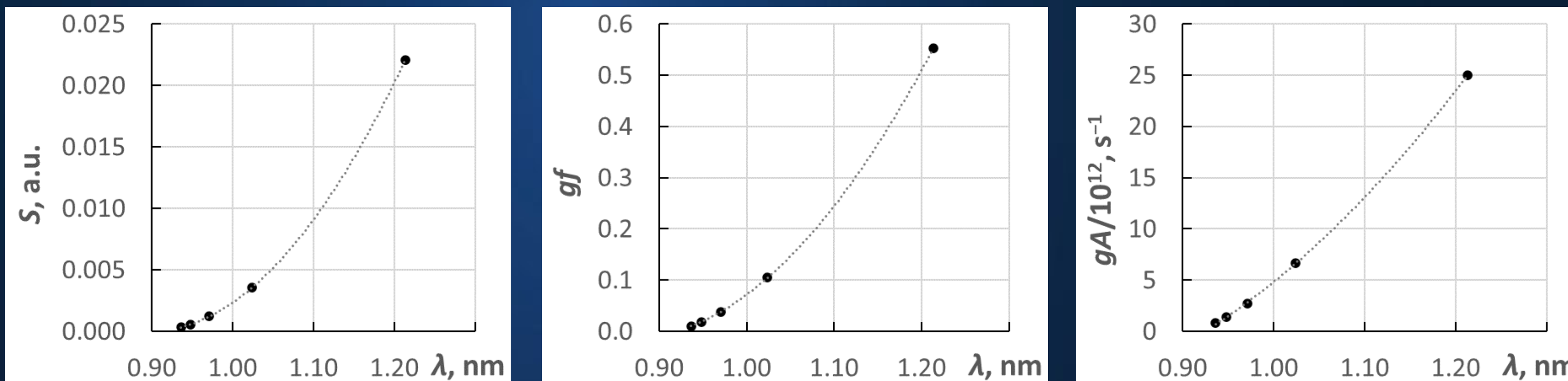
$$S^{\mathrm{e}}_{\alpha\beta}(B) \propto \left[\int_0^\infty R_\alpha R_\beta r^L \mathrm{d}r\right]^2$$

Electric transitions, Coulomb gauge:

$$S^{\mathrm{e}}_{\alpha\beta}(C) \propto \frac{1}{\omega^2}\left[\int_0^\infty R_\beta \left\{\frac{\mathrm{d}}{\mathrm{d}r} + \frac{(l_\alpha - l_\beta)(l_\alpha + l_\beta + 1)}{2r}\right\} R_\alpha \mathrm{d}r\right]^2$$

Dividing transitions into groups
Which parameter does not depend on energy?

Example: resonance lines of H-like ions, 1s-$np_{3/2}$, n = 2–6
O. Jitrik, C.F. Bunge, [JPCRD **33**, 1059 (2004)]

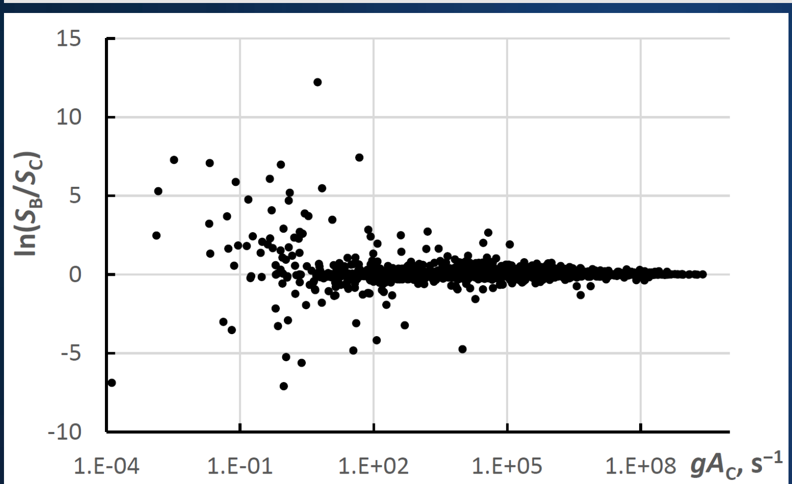


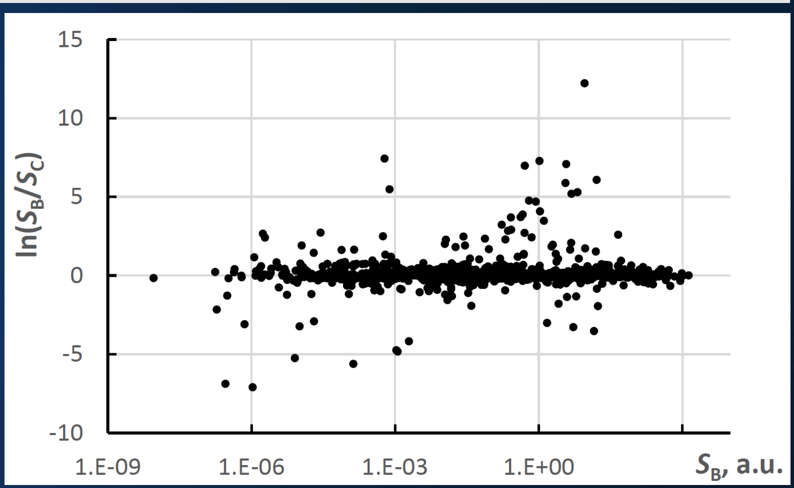
max/min = 69 53 32

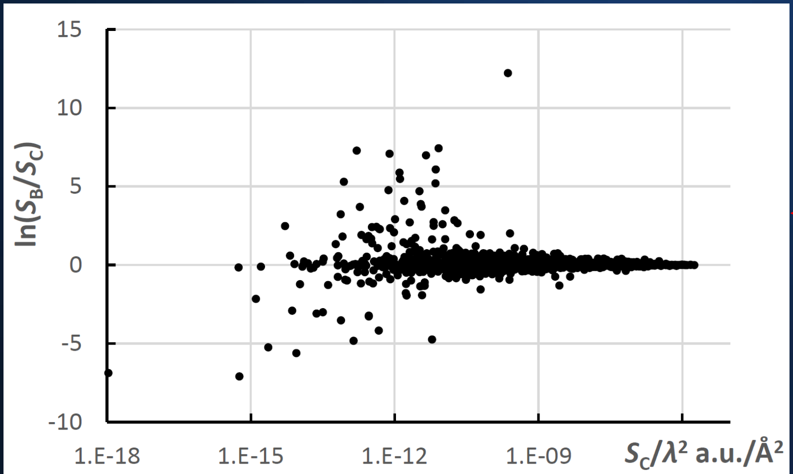
In vast majority of cases, S (length form for electric transitions) is empirically found to correlate best with uncertainties.
However, there are exceptions, so one must check if other quantities are better.

Dividing transitions into groups
Which parameter better correlates with uncertainties?

MCDHF calculation for N I: M.C. Li, W. Li, P. Jönsson et al., ApJS **265**, 26 (2023)







S_C/λ^2 is much better than S_B in this case, but gA_C is better yet.

Gauge dependence

Z. Rudzikas, Theoretical Atomic Spectroscopy (Cambridge Univ. Press, 2007)
X.H. Zhang, G. Del Zanna, K. Wang et al., ApJS **257**, 56 (2021)
P. Rynkun, S. Banerjee, G. Gaigalas et al., A&A **658**, A82 (2022)

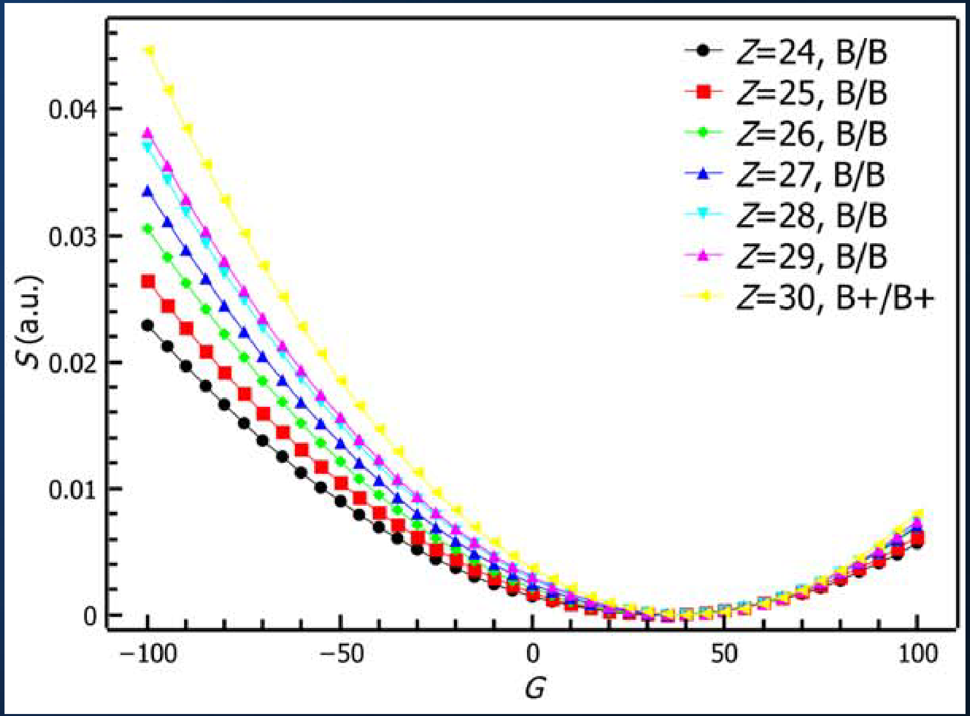
$$S = aG^2 + bG + c$$

$G = 0$ – Coulomb

$G = \sqrt{(L+1)L}$ – Babushkin

$$G_{S=0} = \frac{\sqrt{2}}{1 - (M_B/M_C)}$$

$|G_{S=0}| \gg 1$ – good accuracy



This methodology reflects a belief that $|1 - M_B/M_C|$ is never random and always indicates a real accuracy of a calculation.

Gauge dependence

A. Hibbert, Galaxies **6**, 77 (2018)

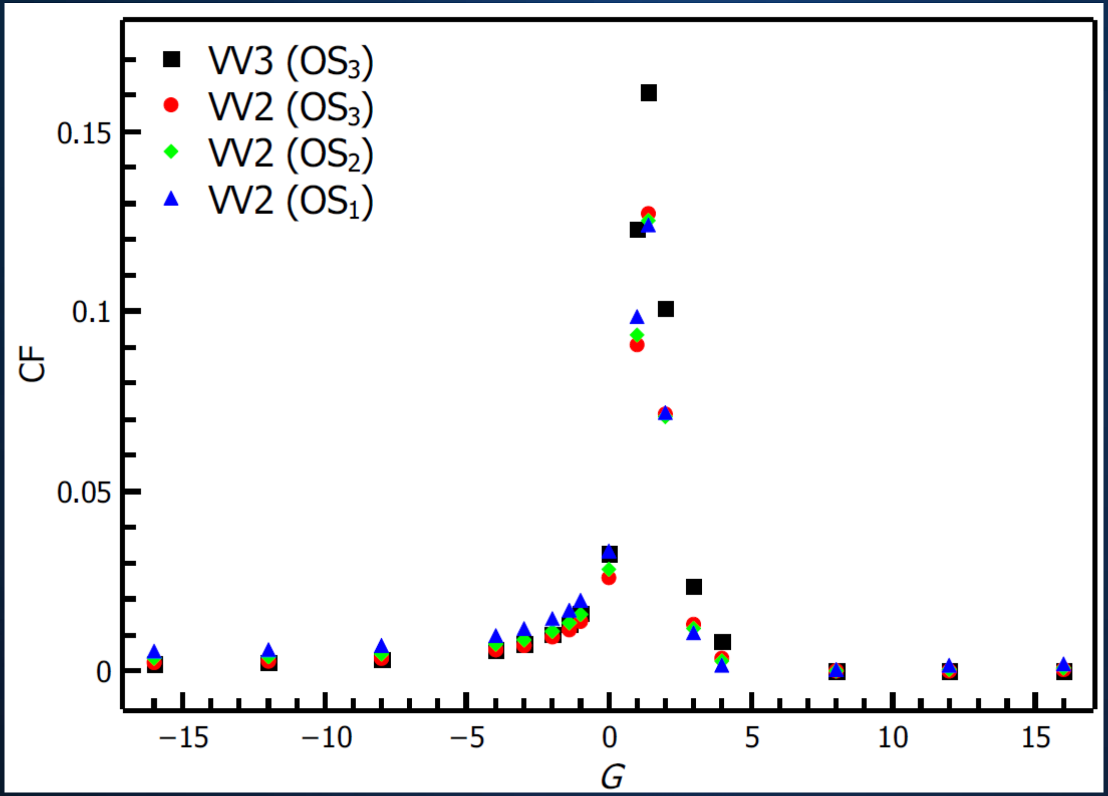
"However, even though exact agreement between the two forms is achieved in a local potential approximation, the common value is not necessarily correct. It is sometimes possible to achieve good length and velocity agreement even in the HF approximation (a non-local potential method), but again the common value can be incorrect."

Methodology needed:

How to distinguish when closeness of S_B and S_C is a computational artifact, and when it reflects the real accuracy?

Cancellation factor

P. Rynkun et al., A&A **658**, A82 (2022)
G. Gaigalas et al., ApJS **248**, 13 (2020)



Ce IV, $5s^2 5p^6 5d\ ^2D_{3/2}$–$4f 5s^2 5p^6\ ^2F^\circ_{5/2}$

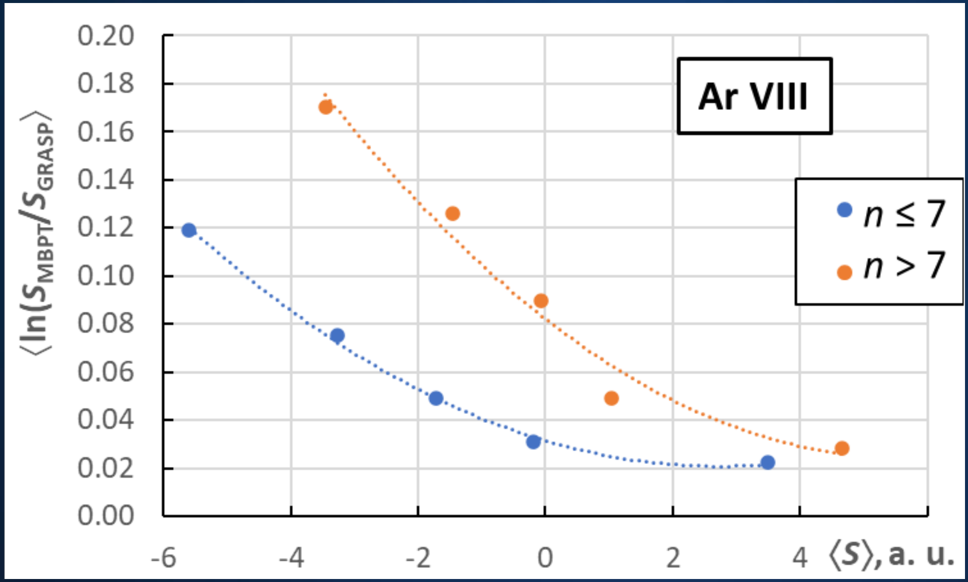
Most transitions have the largest CF (better accuracy) for $G = 1$ or $G = \sqrt{2}$.

The CF calculation should be included in the GRASP package.

M. Bilal et al., PRA **99**, 062511 (2019):
For some transitions, velocity form gives more accurate results!

Dividing transitions into groups:
Account for different amount of correlation effects

S. Rathi and L. Sharma, Atoms **10**, 131 (2022)



GRASP calculations included virtual excitations to $n \leq 11$. Results are given for $n \leq 9$. Configurations with $n \leq 7$ include more correlations than those with $n = 8, 9$.

Transitions expected to have different accuracy must be considered separately.

Uncertainties in computed lifetimes: Comparisons with experiments

No database of critically evaluated lifetimes!

Use the NIST Atomic Transition Probability Bibliographic Database: https://physics.nist.gov/fvalbib

Pay attention to experimental methods: not all are reliable.

Example: beam-foil results using ANDC (newer) are more accurate than ones with simple fitting of decay curves.

Uncertainties in computed lifetimes:
Error propagation

Common error: comparison of τ_{length} and $\tau_{velocity}$

1) M1, M2, etc. are not accounted for.
2) Same problems as with S_{length} and $S_{velocity}$.
3) Contributions from errors in wavelength to *A*-values must be accounted for.

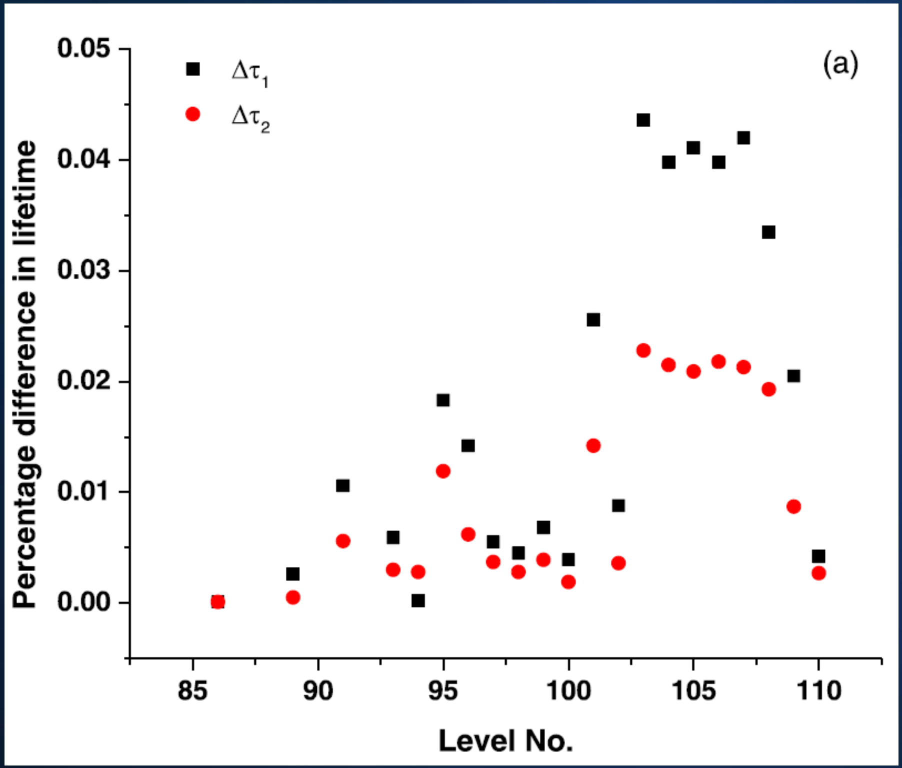
Good practice examples:

M.C. Li et al., ApJS **265**, 26 (2023) (N I); W. Li et al., A&A **674**, A54 (2023) (O I);
S. Rathi and L. Sharma, Atoms **10**, 131 (2022) (Na-like Ar, Kr, Xe);
J. Ruczkowski, M. Elantkowska, JQSRT **277**, 107996 (2022) (Sc II).

$$\frac{u(\tau_i)}{\tau_i} = \tau_i \sqrt{\sum_k u(A_{ik})^2}$$

Uncertainties in computed lifetimes: Alternative method

N. Singh et al., JESRP **257**, 147205 (2022) – W LXXIII and Au LXXVIII (He-like)

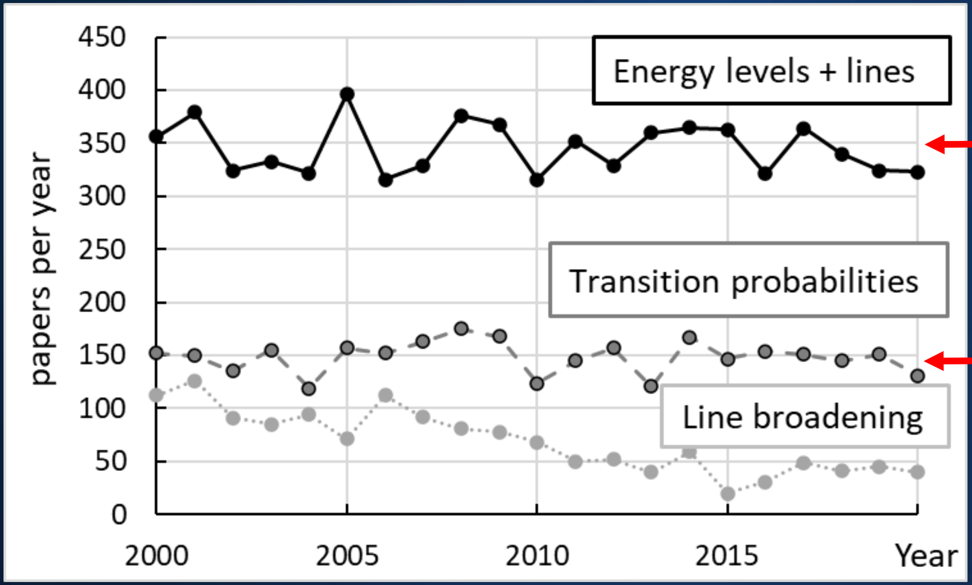


$$\Delta\tau_1 = \frac{\tau_{n=6} - \tau_{n=5}}{\tau_{n=5}}$$

$$\Delta\tau_2 = \frac{\tau_{n=7} - \tau_{n=6}}{\tau_{n=6}}$$

Conclusions and outlook

New papers on atomic spectroscopy keep being published at a rate of 500 per year



Most EL papers are fragmentary. To make data useful, old works must be compiled, and their uncertainties evaluated.

Most TP papers are now theoretical, **90%** do not have uncertainties.
Such publications must be banned.

Progress in methods and new ideas are gratifying but insufficient.
More effort is needed in methods of uncertainty evaluation.